



# Hierarchical TS-1 zeolite as an efficient catalyst for oxidative desulphurization of hydrocarbon fractions

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## ABSTRACT

The catalytic oxidative desulphurization (ODS) of S-containing aromatic compounds has been investigated over a hierarchical TS-1 zeolite prepared from silanized protozeolitic units, characterized by having, additionally to the zeolitic micropores, a secondary porosity within the supermicro/mesopore region. A standard TS-1 sample has been employed as reference catalyst. The influence of both the solvent (*n*-heptane and acetonitrile) and the oxidizing agent (hydrogen peroxide and tert-butylhydroperoxide, TBHP) was first studied using dibenzothiophene (DBT) as model substrate. In all cases, the catalytic activity exhibited by the hierarchical TS-1 was much higher than that obtained with the conventional TS-1 as a consequence of the improved accessibility caused by the presence of the secondary porosity. A very high desulphurization activity was obtained with the combination of heptane and TBHP, as solvent and oxidant, respectively, leading to an almost total DBT conversion. This fact has been attributed to the fully miscibility of the oxidant solution (TBHP in decane) in the organic reaction medium. Moreover, it is noteworthy that, in these conditions, the oxidation product (sulphone) is insoluble in the reaction medium, which facilitates its removal by filtration or centrifugation. Additionally, the oxidation of different aromatic organosulphur compounds [benzothiophene (BT), 2-methylbenzothiophene (2-MBT), 2,5-dimethylthiophene (2,5-DMT) and dibenzothiophene (DBT)] was investigated using the hierarchical TS-1 catalyst. The trend in the conversion values obtained was 2,5-DMT < BT < 2-MBT < DBT. These results indicate that the oxidation conversion is determined by the nucleophilic character of the sulphur atom, and not by the molecular size of the S-containing compound, provided that the steric and diffusional limitations are overcome by the presence of the hierarchical TS-1 porosity.

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## 1. Introduction

The presence of sulphur-containing organic compounds in liquid fuels is one of the most important sources of atmospheric pollution, since after combustion, they lead to SO<sub>x</sub> emissions, which causes important health problems and are precursors of the acid rain. Likewise, the presence of sulphur in fuels provokes corrosion of refining equipment and combustion engines. For that reasons, and in order to minimize the negative health and environmental effects, the legislations currently in force establish that the sulphur concentrations in transport fuels should be lower than 10 ppm [1–5].

Hydrodesulphurization (HDS) is the conventional process for the elimination of organosulphur compounds from liquid fuels, by converting them into hydrogen sulphide. The HDS process is usually conducted over sulphided CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts, whose activity not only depends on the properties of the catalyst, but also on the reaction conditions (temperature, and H<sub>2</sub> partial pressure), reactor type, process design and nature and concentration of the organosulphur compounds present in the feed stream [6]. Crude oil fractions with low boiling points contain mostly aliphatic organosulphur compounds: mercaptans, sulphides and disulphides, which are very reactive in conventional hydrotreating processes, being easily removed from fuel. However, in heavier oil fractions like diesel, thiophenes, benzothiophenes and their alkylated derivatives are predominant. These compounds are more difficult to be removed by HDS than mercaptans and sulphides, demanding higher hydrogen pressures, temperatures and/or contact times to achieve sulphur concentrations in fuels below 10 ppm [2].

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Oxidative desulphurization (ODS) is considered one of the most promising methods for fuel deep desulphurization. In comparison to conventional HDS, ODS can be carried out under mild conditions, employing temperatures lower than 100 °C and atmospheric pressure [7]. Through this technology, sulphur compounds such as thiophene, benzothiophene and their derivatives can be oxidized into the corresponding sulphones by the electrophilic addition of oxygen. Sulphones are highly polarized compounds, which can be removed from oil fractions by simple liquid–liquid extraction using a polar solvent [8]. The oxidation of thiophenic and benzothiophenic compounds with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) has been reported using formic acid [9], acetic acid [10] polyoxometalate [11], molybdenum supported on alumina [12] and titanium microporous molecular sieves [5,13] as catalysts. However, these materials exhibit some drawbacks: formic acid reduces the quality of the liquid fuels, polyoxometalate is difficult to be recovered and regenerated and molybdenum supported catalyst are not very stable, since molybdenum tends to be leached into the reaction medium [14]. The use of titanium-containing zeolites is also limited in ODS due to the restricted access of the bulky sulphur compounds into the zeolitic micropores. In this sense, the oxidation of thiophene and benzothiophene derivatives has been investigated over different micro and mesotitanosilicates using hydrogen peroxide [5,15]. It was found that ordered mesoporous materials such as Ti-MCM-41 and Ti-HSM are very active for the oxidation of bulky sulphur compounds, while TS-1 zeolite was almost inactive, due to the steric and diffusion limitations derived from its microporous nature. However, ordered mesoporous materials suffer from limited hydrothermal stability due to the amorphous nature of their walls, which strongly limits their durability and commercial application [16–18].

In this context, the development of Ti-containing hierarchical zeolites can overcome the limitations presented by single micro- or mesoporous materials. This new type of materials, characterized by having bimodal pore architecture, may combine the catalytic properties and hydrothermal stability of the zeolitic active sites and the enhanced accessibility provided by an additional mesoporosity [19]. The synthesis of Ti-containing hierarchical zeolitic materials, mainly TS-1 zeolite, has been reported following different strategies. Thus, hierarchical TS-1 materials have been obtained by acid and alkaline post-synthesis treatments [20] or using hard-templates such as carbon black, CMK-3 or carbons obtained from sucrose carbonization [21–23]. Likewise, the use of organosilane compounds as soft-templates has been found as a successful strategy to obtain hierarchical TS-1 zeolitic materials [24,25].

In this work, we report the application of hierarchical TS-1 zeolite, synthesized from silanized protozeolitic units, in the oxidation of thiophenic and benzothiophenic organic compounds. The hierarchical TS-1 zeolites so obtained are formed by zeolitic nanounits aggregates, showing a secondary porosity in the supermicro- and mesopore range, additionally to the microporosity typical of MFI-type materials, which provides them with enhanced BET and external/mesopore surface areas. These nanounits are not independent and isolated units, since they present significant intergrowth, providing hierarchical TS-1 with high thermal and mechanical stability, as it was shown in a previous work [26].

Firstly, the effect of the solvent nature (*n*-heptane and acetonitrile) and of the oxidant type ( $\text{H}_2\text{O}_2$ , TBHP) has been explored. In these experiments, dibenzothiophene (DBT) was used as organosulphur model compound. For comparison, the results obtained for a conventional TS-1 zeolite are also shown. Likewise, in order to study the influence of the organosulphur compound nature, the oxidation of different S-containing substrates has been investigated (benzothiophene (BT), dibenzothiophene (DBT), 2-methylbenzothiophene (2-MBT) and 2,5-dimethylthiophene (2,5-DMT)).

## 2. Experimental

### 2.1. Synthesis of hierarchical TS-1 zeolite

The hierarchical TS-1 zeolite (h-TS-1) was prepared according to the protozeolitic units silanization method previously reported by our group [24,26]. Firstly, a synthesis gel, with molar composition of  $1\text{SiO}_2:0.0163\text{TiO}_2:0.44\text{TPAOH}:28.5\text{H}_2\text{O}$ , was prepared following the original recipe developed by Taramasso and co-workers [27]. After that, in order to promote the protozeolitic units generation, this solution was precrystallized in a reflux system under stirring conditions at 90 °C for 24 h. Then, the silanization agent (phenylaminopropyltrimethoxysilane, PHAPTMS, Aldrich) was added with a loading of 8 mol% in regard to the total silica content in the gel, and the mixture was stirred at 90 °C for 6 h. Finally, the crystallization treatment was carried out at 170 °C for 8 h in a Teflon vessel under autogenous pressure using microwave heating radiation. During this last crystallization step, the silanization agent, anchored over the surface of the protozeolitic units, disrupts the crystal growth, hindering partially the zeolitic units aggregation. Additionally, a conventional TS-1 zeolite was also prepared following the synthesis procedure previously described but omitting the precrystallization and silanization steps. In both cases, the solid products obtained after the crystallization treatment were recovered by centrifugation, washed several times with distilled water, dried overnight at 110 °C and calcined in air at 550 °C under static air conditions.

### 2.2. Characterization of the catalyst samples

XRD analyses were performed using  $\text{CuK}\alpha$  radiation with a Philips X'PERT MPD diffractometer using a step size and a counting time of 0.02° and 10 s, respectively. DR UV–vis spectra were collected on a CARY-500 spectrophotometer equipped with a diffuse reflectance accessory. Titanium content of the calcined samples was estimated by means of atomic emission spectroscopy with induced coupled plasma (ICP-AES) analyses using a Varian Vista AX instrument. Ar adsorption–desorption isotherms at 87.3 K were measured with an Autosorb-1 analyzer from Quantachrome instruments, degassing the samples at 573 K for 5 h prior to the analysis. The total surface area was estimated according to the BET method, whereas the pore size distribution and the cumulative volume curve were calculated by applying the NL-DFT model assuming cylindrical pore geometry and employing argon–zeolite as adsorbate–adsorbent kernel in the adsorption branch [28]. Finally, TEM images were taken in a PHILIPS TECHNICAL 20 electron microscope operating at 200 kV and 2.7 Å resolutions. Previously, the sample was dispersed in acetone and a droplet of the suspension was deposited onto a carbon-coated copper grid.

### 2.3. Catalytic tests

The catalytic behaviour of the TS-1 zeolite samples was evaluated in oxidative desulphurization process using benzothiophene (BT, 95%, Aldrich), dibenzothiophene (DBT, 98%, Aldrich), 2-methylbenzothiophene (2-MBT, 97% Aldrich), and 2,5-dimethylthiophene (2,5-DMT, 98%, Aldrich) as model sulphur compounds. The catalytic experiments were carried out at atmospheric pressure in a 50 ml round bottom flask immersed in an oil-heating bath and equipped with a magnetic stirrer. Typically, 5 g of solvent, acetonitrile (99%, Alfa) or *n*-heptane (99%, Sharlau), 0.3 mmol of sulphur-containing organic compound and 12.5 mg of catalyst were put in contact at 80 °C. Then, the oxidizing agent, hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30%, Sharlab) or tert-butylhydroperoxide (TBHP, 5.5 M in decane, Aldrich) was added using an oxidant/S-organic compound molar ratio of 2. The catalytic tests were carried out at reaction times between 0 and 60 min.

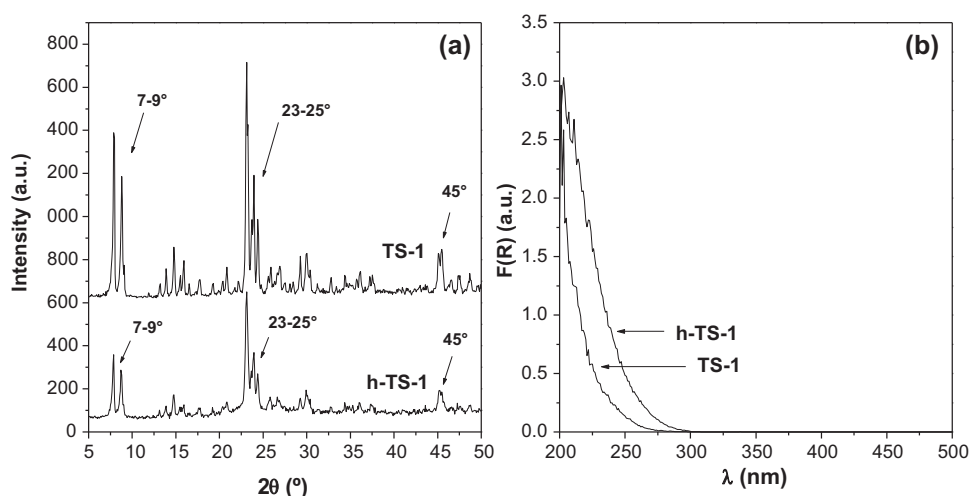


Fig. 1. (a) XRD patterns and (b) DR UV-vis spectra of calcined h-TS-1 and TS-1 zeolites.

The reaction products were analyzed on a Varian 3900 chromatograph equipped with a capillary column (VARIAN CP-SIL 8 CB, 30 m, 0.25 mm i.d., 0.25 mm film thickness) using toluene as internal standard. As carrier gas, He (purity 99.999%) was used with a head column pressure of 10 psi. 1  $\mu$ L of the reaction solution was injected using a split ratio of 65. After an initial 3 min isothermal period, the oven temperature was programmed from 80 to 280  $^{\circ}$ C with a heating rate of 10  $^{\circ}$ C/min. FID and injector temperatures were 330 and 250  $^{\circ}$ C, respectively.

### 3. Results and discussion

#### 3.1. Characterization

XRD patterns of both hierarchical (denoted as h-TS-1) and conventional TS-1 zeolites are shown in Fig. 1(a). Both samples exhibit XRD patterns with diffraction peaks coincident with the MFI zeolitic topology with an orthorhombic symmetry (signals at  $2\theta$  ranged 7–9 $^{\circ}$ , 23–25 $^{\circ}$  and 45 $^{\circ}$ ), showing a high crystallinity degree [27,29]. A significant reduction in the intensity of the diffraction reflections is clearly observed for h-TS-1 material, obtained from silanized protozeolitic units, which is attributed to a reduction in the size of the crystalline domains [24,26]. This result is confirmed by the calculation of the h-TS-1 crystal domain size by means of the Scherrer equation applied to the main diffraction signals. The mean crystal size obtained was around 11.4 nm, which is several times smaller than that observed for the reference TS-1, which exhibit sizes ranged from 250 to 300 nm (calculated through TEM).

Ti atoms coordination in zeolite framework is a relevant aspect since Ti species substituting silicon atoms in the zeolite lattice are the active sites for catalytic oxidations reactions while the existence of extra-framework  $\text{TiO}_2$  has been proved to be detrimental. Fig. 1(b) shows the DR UV-vis spectra of both calcined TS-1 and h-TS-1 zeolites. The spectra are dominated by a characteristic absorption band located at 210–220 nm, originated by

the ligand-to-metal charge transfer in isolated  $[\text{TiO}_4]$  species, which is characteristic of Ti atoms with a tetrahedral coordination. Nevertheless, for the h-TS-1 zeolite, this band spreads out until wavenumber values of 250–260 nm, which is related to the presence of isolated Ti atoms in penta- or hexahedral coordination caused by an increase in the concentration of surface hydroxyl groups or an enhanced hydration capacity [30]. This effect can be interpreted as result of the reduction in the crystalline domain size, previously detected in the XRD analyses. The absence of an absorption threshold at 330 nm implies that both samples are free of non-desired extraframework  $\text{TiO}_2$  phases.

The Ti contents of TS-1 and h-TS-1, estimated by ICP-AES, are shown in Table 1. The titanium weight percentages, 0.99 and 0.93 wt%, and  $\text{Ti}/(\text{Ti} + \text{Si})_{\text{MOL}}$  values, 0.012 and 0.011, obtained for TS-1 and h-TS-1, respectively, are very similar, indicating that both samples possess very similar Ti content. To confirm the crystalline domain size reduction, both TS-1 and h-TS-1 samples were analyzed by TEM (Fig. 2). Thus, the conventional TS-1 zeolite is comprised by regular crystals with mean dimensions in the range of 250–300 nm and well defined edges (Fig. 2(a) and (b)). On the other hand, the h-TS-1 zeolitic material exhibits globular aggregates with sizes around 100–150 nm (Fig. 2(c)). These aggregates are formed by zeolitic nanounits with dimensions in the range 5–10 nm, which corroborates the size reduction of the crystalline domains, previously suggested by the XRD data, and are in agreement with the average crystal domain size determined by the Scherrer method (11.4 nm). These ultrasmall zeolitic nanounits are significantly intergrown, forming crystalline domains with sizes around 15–20 nm, in which the zeolitic nanounits exhibit the same orientation of the diffraction fringes (Fig. 2(d)).

Fig. 3(a) displays the Ar adsorption–desorption isotherms measured at 87 K obtained for both samples. The conventional TS-1 zeolite shows a typical type I isotherm (according to the IUPAC classification) characteristic of pure microporous materials. In contrast, the h-TS-1 sample shows an enhanced adsorption at low and intermediate relative pressures, which suggests the coexistence of

Table 1

Ti content and textural properties of h-TS-1 and TS-1 samples.

Catalyst	Ti wt%	$\text{Ti}/(\text{Ti} + \text{Si})_{\text{MOL}}$	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{ZM}}^a$ ( $\text{m}^2/\text{g}$ )	$S_{\text{SP}}^a$ ( $\text{m}^2/\text{g}$ )	$V_{\text{ZM}}^a$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{SP}}^a$ ( $\text{cm}^3/\text{g}$ )
TS-1	0.99	0.012	427	403	24	0.196	0.121
h-TS-1	0.93	0.011	609	288	321	0.143	0.241

ZM, zeolitic micropores; SP, secondary porosity.

<sup>a</sup> Determined by applying the NL-DFT method.



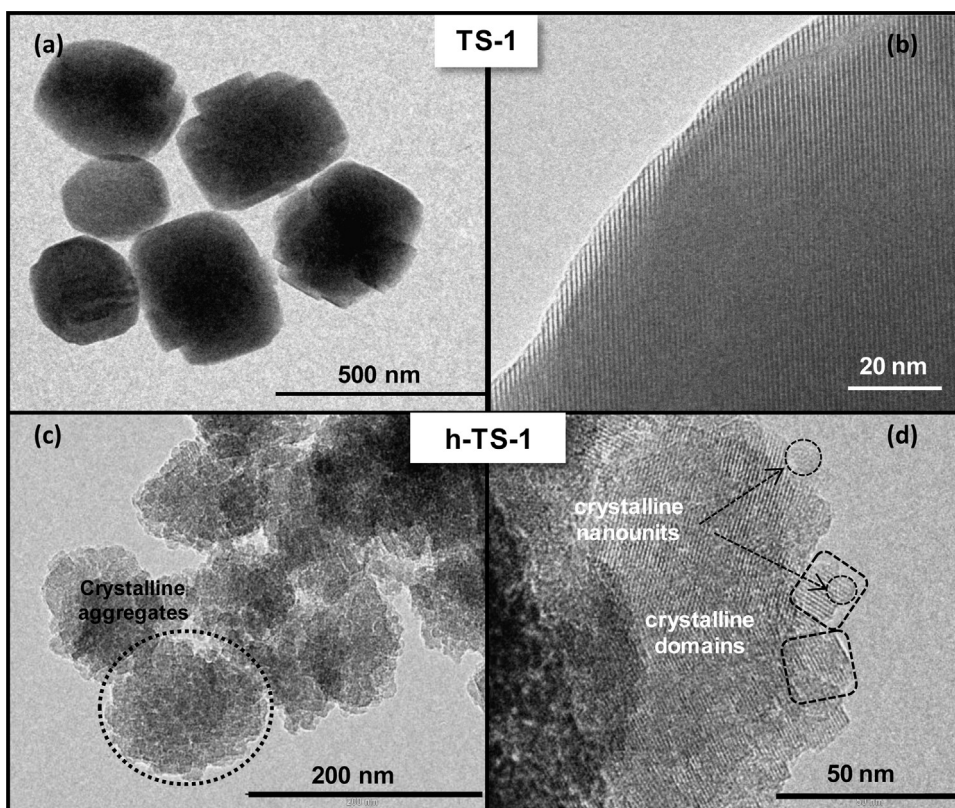


Fig. 2. TEM images of conventional TS-1 (a and b) and h-TS-1 (c and d) zeolites.

micro and mesopores in this material. The cumulative pore volume and pore size distribution curves have been estimated by means of the application of the NL-DFT model (Fig. 3(b)). Both samples exhibit, as expected, a peak at 5.5 Å, corresponding to the MFI micropore size. However, h-TS-1 zeolite shows additional peaks in the range of pore sizes from 15 to 60 Å, corroborating the existence of a secondary porosity in the supermicro/mesopore region. This secondary porosity arises from the voids existing between the interconnected zeolitic nanounits, previously observed through TEM analysis.

Table 1 exhibits the main textural properties of both conventional and hierarchical TS-1 samples. It can be appreciated that the hierarchical TS-1 material exhibits enhanced BET surface area and secondary porosity surface area compared to the conventional TS-1 zeolite, showing values of 609 and 321 m<sup>2</sup>/g, respectively. For this sample the surface attributed to the secondary porosity represents more than 50% of the total specific surface area.

### 3.2. Catalytic activity

Oxidative desulphurization (ODS) is considered as one of the most promising treatments for deep desulphurization of liquids fuels. The advances achieved during the last decade have demonstrated its feasibility to remove sulphur compounds from fuels in order to satisfy the strict environmental regulation limits. Moreover, ODS possesses great advantages compared to HDS: low reaction temperatures and pressures, there is no need of using expensive hydrogen and valid for the conversion of refractory organosulphur compounds, such as thiophenic and benzothiophenic species. Therefore, ODS can be considered a very interesting complementary process that could be coupled to conventional HDS for producing deeply desulphurized light oils [14].

In this study, the catalytic behaviour of both hierarchical and conventional TS-1 zeolites was firstly evaluated using different

oxidizing agents (TBHP and H<sub>2</sub>O<sub>2</sub>) and solvents (acetonitrile and *n*-heptane). For these experiments, dibenzothiophene (DBT) was used as model compound since it is the major sulphur-containing compound present in liquid hydrocarbon fuels. The reaction scheme of the DBT oxidation to yield the corresponding sulphone is shown in Fig. 4.

Fig. 5 displays the catalytic performance of hierarchical and conventional TS-1 zeolites in DBT catalytic oxidation using acetonitrile as solvent. Both H<sub>2</sub>O<sub>2</sub> and TBHP were employed as oxidizing agents in these experiments. As it can be seen, the reference TS-1 sample exhibits very poor catalytic activity using H<sub>2</sub>O<sub>2</sub> and TBHP, showing DBT conversion values below 5%. These results confirm the limited accessibility of bulky molecules (DBT and TBHP) to the titanium active sites located inside the zeolitic micropores. In contrast, the hierarchical TS-1 sample shows high activity in DBT oxidation with both oxidants. The presence of a secondary porosity in h-TS-1 zeolite overcomes the steric and diffusion limitations of conventional TS-1, allowing bulky molecules (DBT and TBHP) to access to the Ti active sites of the zeolite and enabling the DBT oxidation. The catalytic activity is different depending on the oxidizing agent used. Thus, after 1 h of reaction, conversions of 63% and 85% were reached using TBHP and H<sub>2</sub>O<sub>2</sub> as oxidants, respectively. The remarkable catalytic activity obtained with hydrogen peroxide is a surprising result, since in previous works, we have found that the activity of hierarchical TS-1 zeolites in olefin epoxidation was very poor when H<sub>2</sub>O<sub>2</sub> is employed as oxidant. This behaviour has been explained by a reduction of the hydrophobic nature of the zeolite surface owing to the increase in the amount of surface hydroxyl groups located on the surface area of the secondary porosity. As a consequence, water molecules, added together with H<sub>2</sub>O<sub>2</sub>, are adsorbed on the external/mesopore zeolite surface, hindering the access of the olefin (1-octene) to the Ti active sites [31]. However, this effect is not observed in the present work for the DBT oxidation, which may be due to the lower hydrophobic nature of this organic substrate, so

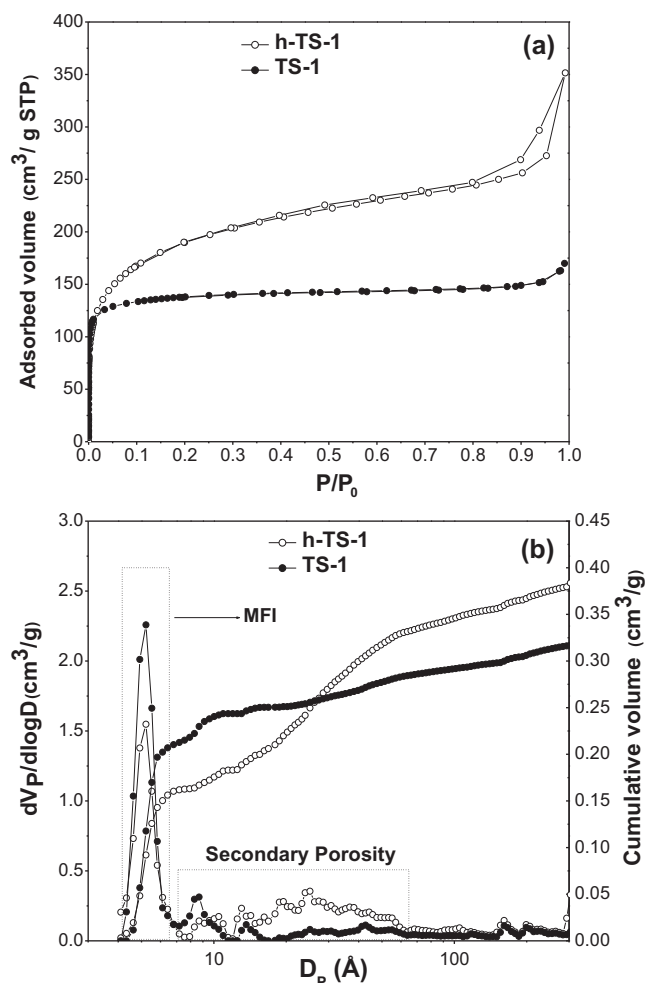


Fig. 3. (a) Ar adsorption-desorption isotherms at 87 K and (b) NL-DFT pore size distributions and cumulative pore volume curves of h-TS-1 and TS-1 samples.

it is less hindered for being transported through the aqueous layer formed over the external/mesopore zeolite surface to reach the Ti sites. On the other hand, the higher conversion obtained with H<sub>2</sub>O<sub>2</sub>, compared to TBHP, can be explained as a result of a synergetic effect between the solvent (acetonitrile) and the oxidizing agent (H<sub>2</sub>O<sub>2</sub>) for this kind of reaction. This synergetic effect has been reported in the literature [5] and attributed to a possible additional reaction between H<sub>2</sub>O<sub>2</sub> and acetonitrile, leading to the formation of peroxyimide acid (R-C(=NH)-O-OH), which would act as an active oxidizing agent of the organic substrate.

The catalytic performance of this materials for ODS has been investigated using also a hydrocarbon (*n*-heptane) as solvent. This is of great interest, as this compound could be considered representative of the hydrocarbons present in the fuels, which would avoid the addition of external solvents. Fig. 6 displays the catalytic results exhibited by both TS-1 zeolites using *n*-heptane as

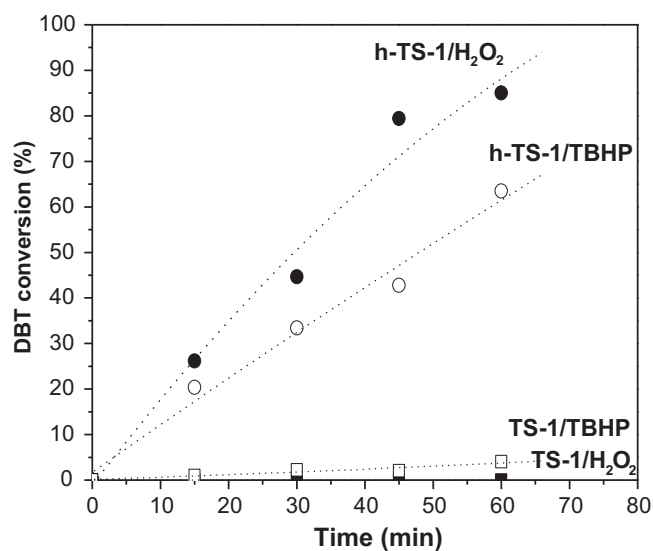


Fig. 5. DBT catalytic oxidation using acetonitrile: (○) h-TS-1/TBHP, (●) h-TS-1/H<sub>2</sub>O<sub>2</sub>, (□) TS-1/TBHP, (■) TS-1/H<sub>2</sub>O<sub>2</sub>.

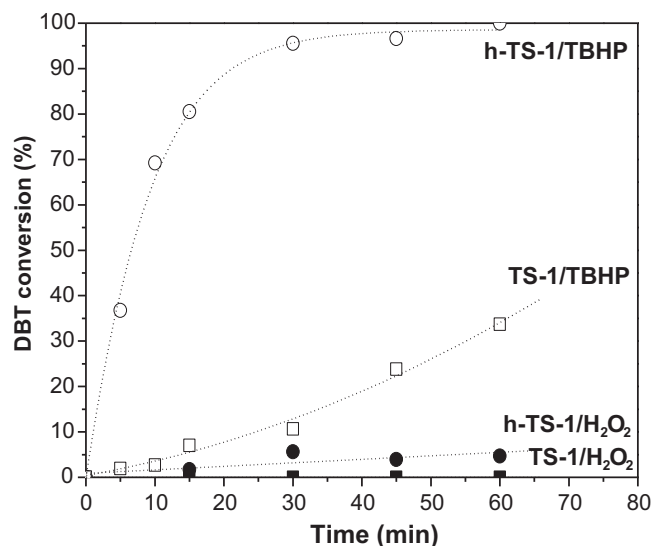


Fig. 6. DBT catalytic oxidation using *n*-heptane: (○) h-TS-1/TBHP, (●) h-TS-1/H<sub>2</sub>O<sub>2</sub>, (□) TS-1/TBHP, (■) TS-1/H<sub>2</sub>O<sub>2</sub>.

solvent. The results obtained indicate that, in this case, the DBT conversion strongly depends on the oxidizing agent employed in the reaction. Thus, when TBHP is used as oxidant, conversions of 100% and 33.7% are attained for the hierarchical and conventional TS-1, respectively. However, the conversion is almost negligible for both catalysts when H<sub>2</sub>O<sub>2</sub> is used as oxidant. This remarkable difference can be explained taking into account the solubility of TBHP and H<sub>2</sub>O<sub>2</sub> in the *n*-heptane based reaction media. Thus, the TBHP chemical used in the reaction is a TBHP solution in decane (5.5 M).

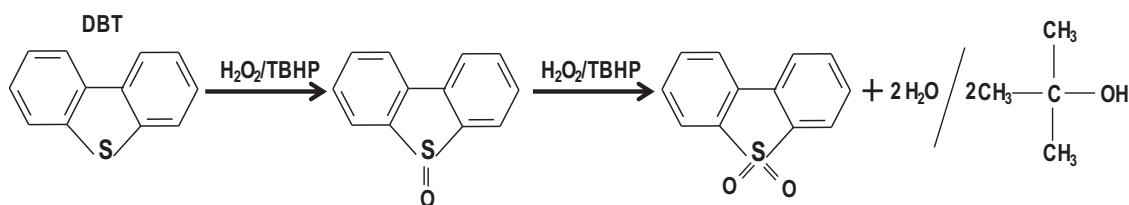


Fig. 4. DBT oxidation reaction using TBHP or H<sub>2</sub>O<sub>2</sub> as oxidants.

This solvent exhibits quite similar polarity that heptane, making the oxidant solution fully miscible in the reaction media. Accordingly, a biphasic reaction medium, comprised by an organic liquid phase (heptane, decane, TBHP and dissolved DBT) and the solid catalyst is obtained. In this case, the catalytic activity depends on the nature of the Ti active sites and the accessibility of both substrate and oxidant to them. However, when  $\text{H}_2\text{O}_2$  is used as oxidant, a triphasic system is formed. In this way, a liquid aqueous phase, ( $\text{H}_2\text{O}_2$  solution) + non-polar organic liquid phase (heptane) + solid catalyst, are present in the reaction medium, DBT being preferentially distributed in the organic phase while the oxidizing agent ( $\text{H}_2\text{O}_2$ ) is in the aqueous phase. This fact is expected to lead to a limited contact between oxidant and substrate molecules, hindering the oxidation reaction.

Concerning the experiments carried out using TBHP, it should be highlighted the excellent catalytic results exhibit by the hierarchical TS-1, which achieved a conversion of 95% after only 30 min of reaction, and a total conversion after 1 h. These results indicate that, in the reaction conditions here employed, the DBT oxidation is favoured and occurs very fast, attaining very high conversions in the first 15–30 min of the reaction time. This activity is enhanced in comparison to the conventional TS-1, which shows a 33% DBT conversion after 1 h, which can be associated to the restricted access of the substrate and oxidizing agent into the zeolitic micropores and the low proportion of accessible active sites, which are present over the external surface of the zeolite. Using the data at short reaction times, the initial reaction rate has been estimated for both zeolites, resulting in  $2.46 \times 10^{-3}$  and  $0.169 \times 10^{-3} \text{ mol l}^{-1} \text{ min}^{-1}$  for h-TS-1 and conventional TS-1, respectively. According to these values, the initial reaction rate is 14.5 times faster for the hierarchical sample than in the reference one. This ratio is quite similar to the one existing between the respective external/mesopore surface areas ( $321 \div 24 \text{ m}^2/\text{g} = 13.4$ ). These results confirm that the DBT oxidation only occurs over the non-sterically hindered surface of the zeolite catalysts, whereas the contribution of the zeolitic micropores is negligible. For the hierarchical TS-1, it corresponds to the surface associated to the secondary porosity and, in the conventional TS-1, it refers to the external surface of the zeolite crystals.

The DBT conversion here obtained over h-TS-1 is higher than that reported in the literature using a silylated Ti-MCM-41 as catalyst, which shows a conversion percentage of 11% after 30 min of reaction [32]. This higher activity can be related to the crystalline nature of titanium active sites in h-TS-1 zeolite in contrast

to the amorphous Ti environment of the Ti-MCM-41 material. However, the use of different experimental conditions should be also considered, since in that work a TBHP aqueous solution was used as oxidizing agent. Yang et al. reported the DBT oxidation of mesoporous TS-1 using cumene hydroperoxide as oxidant. They obtained a DBT conversion value 85% after 60 min of reaction time. Although this conversion percentage is quite high, it must be taken into account that the oxidant/S molar ratio used was several times higher than that employed in the present work (15/1 vs 2/1). Accordingly, the intrinsic activity so obtained is lower than the one here reported over h-TS-1 prepared from silanized protozeolitic units [33].

In summary, the previous results probe that the reaction system formed by *n*-heptane/TBHP/h-TS-1 represents the optimum combination of solvent, oxidant and catalyst for DBT oxidation. As above indicated, *n*-heptane could be considered as representative of the hydrocarbons present in oil fractions and, in this medium, the utilization of TBHP, fully miscible, allows the DBT oxidation to be carried out avoiding the utilization of external solvents, that would be required when diluted  $\text{H}_2\text{O}_2$  is used as oxidant [34–37]. Moreover, the use of h-TS-1 as catalyst enables the complete oxidation of DBT, in spite of being a bulky sulphur-containing aromatic compound.

It is important to point out that, in all the reactions tested, the catalytic oxidation of DBT employing both TBHP and diluted  $\text{H}_2\text{O}_2$  as oxidants led to the corresponding sulphone (1,1-dioxide) as the sole product and tert-butyl alcohol and water, respectively, as the stoichiometric by-products. No traces of sulfoxide were detected among the oxidation products, which can be attributed to the faster sulphone formation from the sulfoxide generated in the first step of the reaction [14]. Likewise, it should be highlighted that, when *n*-heptane is used as solvent, the oxidation product (sulphone) was insoluble, being precipitated from the reaction medium, which facilitates its subsequent separation by filtration or centrifugation. This excellent behaviour of TBHP in the ODS process has been previously reported in the literature using amorphous catalysts such as  $\text{MoO}_x/\text{Al}_2\text{O}_3$  or  $\text{MoO}_x/\text{SiO}_2$  [36–39]. However, the application of the reaction system TBHP-zeolitic catalyst (TS-1) is reported here for the first time.

Once it has been shown that hierarchical TS-1 zeolite is highly active for the catalytic oxidation of DBT, this material was also evaluated for the oxidation of additional S-containing organic compounds: benzothiophene (BT), 2-methylbenzothiophene

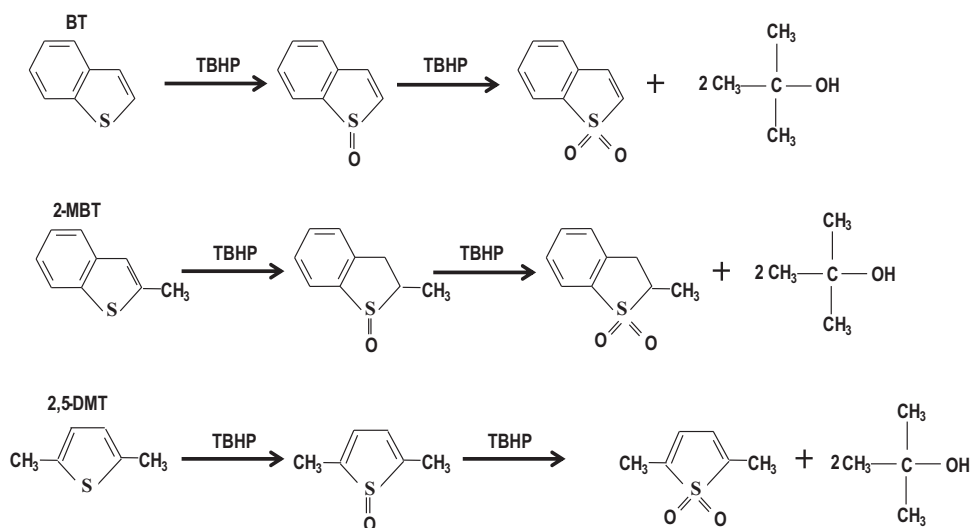


Fig. 7. TBHP oxidation reactions of different S-containing organic compounds.

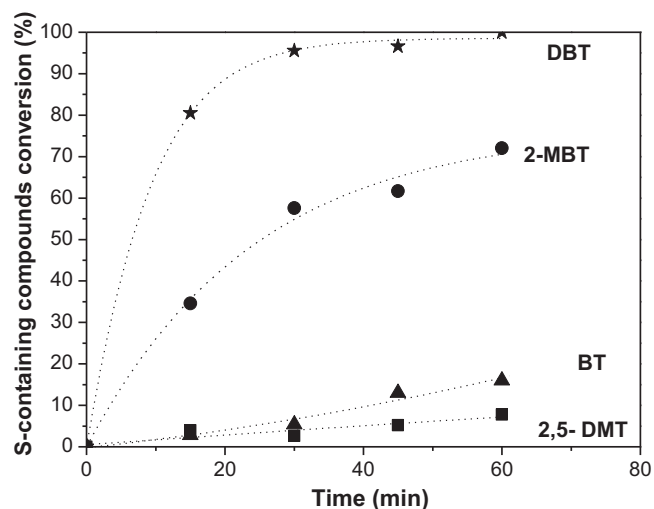


Fig. 8. Catalytic tests for the oxidation of different S-containing compounds with TBHP using h-TS-1: (★) DBT, (●) 2-MBT, (▲) BT, (■) 2,5-DMT.

(2-MBT) and 2,5-dimethylthiophene (2,5-DMT). It has been previously reported that the reactivity of organosulphur compounds in regard to catalytic oxidation may depend also on the nucleophilic character of the sulphur atom [14,34]. In this sense, it has been estimated the electron densities of the sulphur atoms by molecular orbital (MO) calculations [34]. The results obtained by these authors indicate that the nucleophilic character of the sulphur compounds here investigated varies according to the following order: 2,5-DMT < BT < DBT. Although the electron density of 2-MBT was not reported, it can be assumed that the value of this parameter is higher in the methyl-substituted compound (2-MBT) than in the non-substituted one (BT).

The reaction schemes corresponding to the oxidation of these molecules are shown in Fig. 7. These experiments were carried out using *n*-heptane and TBHP as solvent and oxidizing agent, respectively, the results obtained being plotted in Fig. 8. The lowest catalytic activity is obtained for 2,5-DMT, showing a lower conversion than those attained for the condensed aromatic thiophenes (BT, 2-MBT and DBT). This is an expected result due to the scarce reactivity of the thiophenic compounds. This fact is due to the low nucleophilic character of the sulphur atom in these molecules, since its electron pair participates in the aromatic delocalization and, therefore, it is less available for electron donation [14,34]. The conversion values corresponding to the benzothiophenic compounds follow the trend: BT < 2-MBT < DBT, which agrees well with the order of their nucleophilic character. It is remarkable that the highest conversion is obtained for DBT, which is the compound exhibiting the largest molecular size. These results denote that, when steric and/or mass transfer limitations are not expected, like it occurs when the hierarchical TS-1 zeolite is employed as catalyst, the catalytic activity for the organosulphur oxidative conversion is governed by the nucleophilic character of the sulphur atom of the S-containing compound and not by the accessibility of the substrates towards the Ti active sites.

#### 4. Conclusions

Hierarchical TS-1 zeolite, prepared by silanization of protozeolitic units, has been probed as an efficient and highly active catalyst for the oxidation of organosulphur compounds. This excellent activity is obtained thanks to the presence of a secondary porosity in the micro-mesopore range, which facilitates the accessibility towards the Ti active

sites in spite of using bulky substrates and oxidants. The influence of solvent (acetonitrile and *n*-heptane) and type of oxidant ( $H_2O_2$  and TBHP) has been studied. The best results have been obtained when using *n*-heptane as solvent and TBHP as oxidant, which allowed obtaining a total DBT conversion. This excellent result has been attributed to the complete solubility of the organic oxidant solution (TBHP in decane) in the *n*-heptane based reaction medium. Since *n*-heptane can be considered as representative of the hydrocarbons present in oil fractions, these results demonstrate the possibility to carry out the ODS process without adding any external solvent, which would be required when diluted  $H_2O_2$  is used as oxidant.

Additionally, the influence of the type of the sulphur compound has been also investigated. It has been found that benzothiophenic compounds (BT, DBT and 2-MBT) are more easily oxidized than thiophenic derivatives (2-DMT) owing to the low nucleophilic character of the sulphur atom in this last type of compounds. Likewise, among the benzothiophenic compounds explored, the conversion degree is governed by the nucleophilic character of the S atom of the organosulphur compound (BT < 2-MBT < DBT) provided that hierarchical TS-1, largely free of steric and mass transfer limitations, is employed as catalyst.

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